Indian J. Phys. **75A** (4), 297-300 (2001)

IJP A
an international journal

Magnetism Department at IACS : Krishnan's creation

C K Majumdar*
INSA Senior Scientist, Physics and Applied Mathematics Unit,
Indian Statistical Institute, 203 B T Road, Calcutta-700 035, India

Abstract : Krishnan started his physics research in spectroscopy with C V Raman and did some pioneering work in Raman effect in solids Later he developed precise experimental methods to measure magnetic anisotropy in crystals ; these methods went by the names *the oscillation method* and *the critical couple method*. Some important results will be recalled The work of Krishnan and his students and coworkers established the usefulness of magnetic methods as a supplement to X-ray methods for determining crystal structure This led to the organisation of the Department of Magnetism in the Indian Association for the Cultivation of Science (I A C S) We shall examine some things which their work missed, and also subsequent developments in the field of magnetism.

Keywords Magnetic anisotropy, magnetic susceptibility , antiferromagnetism

PACS Nos. 75 30 Gw, 75.30 Cr

1. Introduction

K. S. Krishnan started research in spectroscopy with C. V. Raman [1, 2] He was associated with the discovery of Raman Effect [3]; he published some pioneering results for Raman effect in solids [4] Then at the Dacca University (now in Bangladesh) and later at I A C S, Krishnan and his students developed precise experimental methods and measured magnetic anisotropy in crystals. There methods were called the oscillation method and the critical couple method. Their work led to the organisation of Magnetism Department at I A C S. These measurements established the usefulness of the magnetic methods as a supplement to X-ray methods for determining crystal structure [1]. The voluminous data also provided some experimental basis of the crystal field theory. We shall recall some interesting results. We shall also point out that Krishnan and his students missed discovering antiferromagnetism. Some remarks on subsequent developments in the field of magnetism will be made to put the work in modern perspective.

2. Crystal magnetism

The magnetic energy of a crystalline substance can be written as [5] :

$$E = -\frac{1}{2}\int\left[k_{1,1}H_x^2 + k_{2,2}H_y^2 + k_{3,3}H_z^2 + 2k_{1,2}H_xH_y + 2k_{2,3}H_yH_z + 2k_{3,1}H_zH_x\right]dv, \quad (1)$$

where k_{ij} are the components of the susceptibility tensor of the crystal referred to the coordinates x, y, z and the integral is taken over the whole volume of the crystal whose shape is yet to be specified. If the applied field is in the x direction, $H_y = H_z = 0$ and the energy is

$$E = -\frac{1}{2}\int k_H H^2 dv, \quad (2)$$

where k_H is the susceptibility of the crystal in the x direction and depends on the direction x of H. The energy of the crystal cannot depend on the choice of axes, so

$$k_{1,1}H_x^2 + k_{2,2}H_y^2 + \ldots\ldots + 2k_{1,2}H_xH_y + \ldots\ldots = k_H H^2. \quad (3)$$

If (l_1, m_1, n_1) are the direction cosines of H relative to the coordinates (x, y, z), we get

$$k_{1,1}l_1^2 + k_{2,2}m_1^2 + \ldots\ldots + 2k_{1,2}l_1m_1 + \ldots\ldots = k_H. \quad (4)$$

We may refer the magnetic ellipsoid to its principal axes which are defined by $k_{1,1} = k_1$, $k_{2,2} = k_2$, $k_{3,3} = k_3$, $k_{1,2} = k_{2,3} = k_{31} = 0$,. k_1, k_2, k_3 are termed the principal magnetic susceptibilities. Now if H is in the direction (l, m, n) with regand to the principal axes, we get

$$k_1l^2 + k_2m^2 + k_3n^2 = k_H. \quad (5)$$

Corresponding to the volume susceptibilities k_1, k_2, k_3 we have mass susceptibilities χ_1, χ_2, χ_3, respectively. Measurement

* Deceased

with powdered samples gives us $\frac{1}{3}(k_1+k_2+k_3)$ or $\frac{1}{3}(\chi_1+\chi_3+\chi_2)$.

If often happens that in the case of a monoclinic crystal, the direction of only one principal magnetic axis k_3 is known. If the crystal is mounted with the k_3 axis parallel to the z axis and perpendicular to H, then $n=0$ and (5) gives

$$k_1 l^2 + k_2 m^2 = k_H$$

or

$$k_1 \cos^2\phi + k_2 \sin^2\phi = k_H, \tag{6}$$

where ϕ to the angle between the k_1 axis and H. A couple, equal to the rate of change of magnetic energy with angle of displacement $dE/d\phi$, will act on the crystal :

$$\frac{dE}{d\phi} = -\frac{1}{2}\frac{d}{d\phi}(k_H H^2 v) = \frac{1}{2}(k_1-k_2)vH^2 \sin 2\phi. \tag{7}$$

When a circular disc of the crystal is cut with the plane of the disc perpendicular to the known magnetic axis and suspended with the plane horizontal and parallel to a uniform field H, the disc will be acted upon by a couple given by eq. (7) which is maximum for $\phi = \pi/4$.

3. Experimental methods

(a) The oscillation method [6] :

Suppose that a crystal is suspended by a torsion fibre parallel to the k_3 axis and oscillates with a period T_0. The torsion constant is C. If now a uniform field H is applied parallel to the k_1 axis, then from eq. (7) the restoring couple changes from $C\delta\phi$ to $(C+(k_1-k_2)H^2v)\delta\phi$ and a new period T_1 is observed. Then

$$CT_0^2 = \left[C+(k_1-k_2)H^2v\right]T_1^2 \tag{8}$$

or

$$k_1-k_2 = \frac{T_0^2-T_1^2}{T_1^2}\frac{C}{H^2}\cdot\frac{I}{v} \tag{9}$$

For *gm* molecular susceptibility, we get

$$\chi_1-\chi_2 = \left[\left(T_0^2-T_1^2\right)/T_1^2\right].(C/H^2)(M/m) \tag{10}$$

where m is the mass of the crystal and M the molecular weight.

The crystal was attached to the lower end of a short piece of glass suspended by a quartz fibre from a torsion head. Complications from the shapes of the specimens were attended to. Special attention was given to ensure the uniformity of the magnetic field (~ 5kG).

(b) The critical couple method [8] :

The crystal is suspended in a uniform horizontal magnetic field at the end of a calibrated long, thin quartz fibre. The upper end of which is fixed to the axis of a graduated torsion head. The crystal is allowed to take up its equilibrium orientation in the field under zero torsion of the fibre. If the torsion head is now slowly rotated through an angle α, the crystal will rotate in the same direction but through a smaller angle $(\alpha-\phi)$. The couple acting on the crystal tending to restore it to its original orientation would be equal to $\frac{m}{2M}\cdot\Delta\chi H^2 \sin 2\phi$ according to eq. (7), where $\Delta\chi$ is the difference between the maximum and minimum *gm* molecular susceptibility of the crystal in the horizontal plane. This couple is balanced by that due to the torsion fibre viz. $C(\alpha-\phi)$. As the torsion head is rotated further, there comes a stage when ϕ just reaches the value $\pi/4$ (the corresponding value of α being α_c, say) and the couple due to the magnetic field reaches its maximum value. Equating the opposite couples, we get

$$C(\alpha_c-\pi/4) = \frac{m}{2M}\Delta\chi H^2. \tag{11}$$

With the slightest further rotation of the torsion head, the crystal will naturally yield and turn around. On this property is based an accurate measurement of α_c, which by eq. (11) enables us to determine $\Delta\chi$.

(c) Other methods :

To measure an individual component, say the largest principal susceptibility, or the average susceptibility, other standard methods such as the Rabi immersion method [5] were used. These depend on the following fact. On exciting an inhomogeneous magnetic field the force on a small crystal of volume of v is

$$k_H vH(H/dx). \tag{12}$$

A paramagnetic substance tends to move to a higher field. By measuring the force, the susceptibility can be measured.

4. Some interesting results

In a series of six papers [6-11], Krishnan and his students published voluminous data and established the idea that the magnetic anisotropy of a diamagnetic or paramagnetic crystal could be correlated with the anisotropy of the individual molecules and their relative orientations. In favourable cases, the precise orientation of molecules in the unit cell could be determined from magnetocrystalline measurements.

A very interesting measurement was that of the very weak anisotropy of the Mn^{2+} ion in ${}^6S_{5/2}$ state, which was about 0.1% of the mean susceptibility [9]. In the first approximation, the S state is not affected by the ligand field, but higher order approximation leads to a weakly separated Stark multiplet. The paramagnetic anisotropy is comparable to the shape anisotropy of the crystal and is masked by it. The crystal was immersed in a liquid bath of adjustable volume susceptibility so that the

shape anisotropy could be eliminated. To get reliable anisotropy data on $MnSO_4.(N\ H_4)_2SO_4.6H_2O$, one must account for anisotropy due to the diamagnetism of the crystal and to the mutual influence of the Mn^{2+} ions. The latter was shown to be negligible by making measurements on a series of crystals diluted by diamagnetic isomorphs containing *Mg* or *Zn*. To eliminate the diamagnetic part of anisotropy, measurements were made on some diamagnetic isomorphs, *Mg* or *Zn* replacing *Mn*, and also on crystals with different replacements of the monovalent ion NH_4 and of SO_4 by SeO_4. Small variations in diamagnetic anisotropy occur only when the monovalent ion or the SO_4 group is replaced, but the replacement of the bivalent atom *Mn* does not affect diamagnetic anisotropy. With all the corrections made the true anisotropy was determined ; this could predict the temperature variation of specific heat and entropy of the crystal at 0.1 K which was found from adiabatic demagnetization experiments.

Many salts of the rare earths were crystallized and their anisotropy determined [10]. Such a large volume of data was useful in checking the crystal field theory that was being developed by Van Vleck, Penney and Schlapp. A very interesting example was the corroboration of Van Vleck's prediction of level inversion between the Stark levels of six coordinated (octahedral) and four coordinated (tetrahedral) Co^{2+} ions in crystals. The lowest level in the octahedral situation is a triplet, that in the tetrahedral a singlet. Consequently, the red salts of the octahedral Co^{2+} were found to be quite anisotropic, the blue salts Cs_2CoCl_4 and Cs_3CoCl_5 showed very weak anisotropy. Another important work was the magnetic anisotropy study of copper sulphate pentahydrate in relation to its triclinic crystal structure [12].

5. Things missed

Most of the measurements of Krishnan and his students were carried out at room temperature. Only in the last of the series of six papers (in 1939), a low temperature cryostat was described and some measurements at liquid oxygen temperature (90 K or – 183° C) were attempted [11]. The lack of such a facility and not much attention to the temperature variation of susceptibility were the reasons why the Calcutta group missed the very interesting phenomenon of antiferromagnetism, already proposed by Néel and Landau [13].

The susceptibility of a ferromagnetic material follows at high temperature, the Curie Weiss law :

$$\chi = \frac{}{T-\theta}. \tag{13}$$

In antiferromagnets [14], susceptibility has a negative Weiss temperature

$$\chi_A = \frac{}{T+\theta} \tag{14}$$

The inverse susceptibility $\frac{1}{\chi_A}$ would be a straight line with a negative intercept on the temperature axis in the absolute scale. Later experiments show that χ in an antiferromagnet, goes through a maximum at $T(\chi_{max})$: then parallel susceptibility goes towards zero as temperature diminishes, but the perpendicular susceptibility remains a constant ; the susceptibility of a polycrystalline sample diminishes to two-thirds of this constant value; the thermodynamic transition occurs at a temperature T_c slightly below $T(\chi_{max})$. T_c has no relation to θ. In the approximate mean field theory $T_c = T(\chi_{max})$ and the qualitative features are the some.

In their studies of rhodochrosite $MnCO_3$ in 1938 [15], Krishnan and Banerjee measured the susceptibility from 301.5 K to 531.8K (temperatures higher than room temperature) and on plotting $\frac{1}{\chi}$ against T (Figure 1 of the paper) found that the values lay on a straightline and therefore

$$\chi = \frac{3.81}{T+13} \tag{15}$$

They remarked : *Since the temperature range in our measurements is not large, the values obtained here for* θ *and the magnetic moment of* Mn^{2+} *should be regarded as only approximate : our value for* θ *namely–* 13° *practically the same as that deduced by Van Vleck and Penney from the temperature variation of the Verdet constant of the crystal.* A signature for antiferromagnetism was seen, it was not followed up.

The measurement on $CuSO_4.5H_2O$ by Krishnan and Mookherjee was not decisive either [12]. It is known now [16] that this salt shows antiferromagnetic exchange constant J/K = – 1.45 K and transition below 0.03K : this could not be ascertained from their data.

We must also note the uncanny perfection reached by the workers in Krishnan's group in the art of crystal growing. Crystal growth is a part of technology and nowadays there are journals devoted to the subject. Not enough record seems to have been kept for the crystal growth by the group : this is a loss to indigenous technology.

6. Subsequent developments

Krishnan's magnetism group at Calcutta broke up with his departure to Allahabad university (1942) and the temporary closure of I A C S during World War II. His measurements started in a small university department and were done with an apparatus not very expensive. Subsequent developments were somewhat unfavourable to universities.

Firstly, the magnetic phenomena require high field and liquid helium or even lower – millikelvin – temperatures. Perfect diamagnetism is found in superconductors. Superconducting magnets based on type II superconductors can produce very high steady fields ; superconducting quantum interference devices (SQUIDs) are very sensitive measuring devices. These are generally beyond university departments. Some universities and IITs have procured vibration magnetometers and carried on research in magnetic materials.

Secondly, magnetic structure determination took a new turn with the introduction of neutron methods. Neutron diffraction and neutron scattering methods can be done in the vicinity of nuclear reactors. Universities, even research institutions, could not carry out such experiments ; they can collaborate with research groups at the reactors under the Department of Atomic Energy.

Thirdly, research on nuclear moments, much smaller than atomic moments, started with atomic and molecular beams and later gave rise to nuclear magnetic resonance methods. The sophisticated instruments require high technology. Several research groups have procured such facilities and done good work.

The experimental work in magnetism tends to concentrate on sophisticated instruments which can be made available at a few places in India, but the standard set by Krishnan and his students has not been surpassed or equalled.

References

[1] *Collected Works of K S Krishnan* (New Delhi) (1988)

[2] *Indian J. Phys.* **B 73 S** December (1999) (Special issue published on the occasion of the birth centenary of Prof K S Krishnan)

[3] C V Raman and K S Krishnan *Indian J. Phys.* **2** 399 (1928)

[4] K S Krishnan *Indian J. Phys.* **4** 131 (1929)

[5] L F Bates *Modern Magnetism* (Cambridge) (1951)

[6] K S Krishnan, B C Guha and S Banerjee *I. Phil. Trans.* **A231** 235 (Ref. [1] p 308) (1933)

[7] K S Krishnan, N C Chakravorty and S Banerjee *II. Phil Trans* **A232** 99 (Ref. [1] p336) (1933)

[8] K S Krishnan and S Banerjee *II. Phil. Trans.* **A234** 265 (Ref [1] p400) (1935)

[9] K S Krishnan and S Banerjee *IV Phil. Trans.* **A235** 343 (Ref [1] p453) (1936)

[10] K S Krishnan and A Mookherji *V. Phil. Trans.* **A237** 135 (Ref [1] p516) (1938)

[11] K S Krishnan and A Mookherji and A Bose *VI. Phil. Trans.* A238 125 (Ref. [1] p578) (1939)

[12] K S Krishnan and A Mookherji *Phys. Rev.* **50** 860 (Ref. [1] p494) (1936) ; *Phys. Rev.* **54** 533 (Ref. [1] p553) (1938)

[13] L Néel *Ann. Phys.* [10] **18** 5 (1932) ; L Landau *Physik. Z Sowjetunion* **4** 675 (1933) , J H Van Vleck *J Chem Phys* 9 85 (1941)

[14] P W Anderson *Solid St. Phys.* **14** 99 (1963)

[15] K S Krishnan and S Banerjee *Z Kristallogr. Kristallgeom* A99 499 (1938)

[16] L J de Jongh and A R Miedema *Adv. Phys* **23** 1 (1974)